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# **Synergistic fire-retardancy properties of melamine coated ammonium poly(phosphate) in combination with rod-like mineral filler attapulgite for polymer-modified bitumen roofing membranes**

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## **Abstract**

A novel intumescent (carbonization, acid donor and foaming) fire retardant that mimics carbon nanotubes was introduced into bitumen roofing and characterized using cone calorimetry as the main analytical tool. The experimental results indicate that 18% (by mass) attapulgite mineral (ATTP) mixed with base bitumen decreased the peak heat release rate per unit area (pHRRPUA) by 10 %. Further, incorporation of melamine coated ammonium polyphosphate (MAPP) decreased the pHRRPUA by 52% and a mixture of these (3:1, ATTP:MAPP) decreased the pHRRPUA by 25% as compared to adding CaCO<sub>3</sub> as a filler. The residual mass loss after the cone test was also improved with up to 3%. The indication of a positive synergistic flame retardant effect of the ATTP-MAPP mixture is supported by thermogravimetric analysis. The addition of this rod-like mineral improved the general fire retardant properties of the base bitumen and increased the viscosity. Therefore, the polymer-modified bitumen with both fire retardant and rheological properties (providing mechanical strength) is a promising novel approach in the design of bitumen roofing membranes.

## **Keywords**

Polymer-modified bitumen; fire retardant; intumescent fire retardant; cone calorimetry; thermogravimetric analysis; melamine coated ammonium polyphosphate

## Introduction

Bitumen is a crude oil by-product that is dark brown to black, almost non-volatile, highly viscous, adhesive, and waterproof at normal temperature. Chemically, it is composed of thousands of small and large aliphatic to aromatic hydrocarbon molecules<sup>1</sup>. Bitumen can be separated into four generic fractions denoted as SARA (saturates, aromatics, resins and asphaltenes)<sup>2</sup>. Bitumen is primarily used as a binder in asphalt road construction and as a waterproofing agent in roofing applications<sup>3</sup>. Upon heating beyond approximately 300°C, bitumen will ignite and the ensuing combustion process releases enough heat to sustain itself while releasing a substantial amount of smoke<sup>4</sup>. There are crucial points that must be considered in the manufacturing of bituminous roofing membranes. For example, viscosity measurements are of critical importance for use and performance reasons<sup>5</sup>. Indeed, a too low viscosity could give poor adhesion. The roofing membranes can catch fire during, for example, heat gun applications and, once a fire has started it is difficult to control due to the very high heat release rate of the material. Therefore, it is of interest to reduce both the ignitability and flammability of bitumen roofing membranes with the addition of fire retardants, which preferably should be environmentally friendly. However, only limited scientific research with focus on flammability of polymer-modified bitumen (PMB) roofing membranes has been conducted. Therefore, the present study was carried out with special emphasis on ignitability and flammability of PMB when used as base material in roofing membrane applications.

Fire retardants can act either in gas phase or in condensed phase or both through at least four known mechanisms: solid-phase heat sink<sup>6,7,8,9</sup> char formation<sup>10</sup> (carbonaceous or siliceous char), gas-phase flame inhibition<sup>11,12</sup> (chemical or radical interference or release of inert gases) and barrier formation (intumescent)<sup>13</sup>. The fire behavior of bitumen can be substantially influenced by the total content of bitumen and the relative amount and the type of fire retardants mixed into it<sup>14,15</sup>.

Also, due to environmental and safety concerns, several fire retardants have been either banned or will be banned in near future<sup>16</sup>. Therefore, it is foreseen that environmentally friendly, halogen-free, and non-toxic fire retardants will increase in popularity. In the present investigation, an attempt was made to prepare a mixture of fire retardants based on rod-like silicate mineral attapulgite as a synergistic agent and melamine coated ammonium poly(phosphate)(MAPP) as an intumescent barrier. Attapulgite (ATTP) ( $\text{Si}_8\text{O}_{20}\text{Mg}_5(\text{Al})(\text{OH})_2(\text{H}_2\text{O})_4 \cdot 4\text{H}_2\text{O}$ ) is a crystalline hydrated magnesium aluminium silicate with very high surface area (due to the high aspect ratio) and unique three dimensional, needle shaped fibrous structures. The mineral itself contains approximately 10-15 % zeolitic (adsorbed) and crystalline (coordinated) water molecules in the channels present inside the needle shaped structures<sup>17</sup>. This mineral has remarkable mechanical and thermal properties that result in the outstanding attributes of ATTP as compared to other fire retardants such as alumina trihydrate (ATH)<sup>16</sup>. ATTP acts as reinforcement and not only improves the mechanical properties of bituminous roofing but also imparts good thermal stability

by releasing water and creating a protective siliceous layer in the early and sustained phase of the fire, respectively<sup>18,19,20</sup>.

In order to assess the effectiveness of the incorporated fire retardants into base bitumen a mass loss cone calorimetry<sup>21</sup> was used for measuring ignition and burning rate. Thermogravimetric analysis (TGA) was used to help interpret the behavior. Moreover, a literature survey showed that only a few scientific studies were carried out focusing on the fire behavior of PMB by using cone calorimetry as a bench scale analytical tool<sup>22,23</sup>.

## **Experimental Preparation**

### **Materials**

An unmodified base bitumen with a density of 0.99-1.1 g/cm<sup>3</sup> was supplied by a roofing material producer. The bitumen base had a penetration of 180/250×10<sup>-1</sup> mm at 25 °C, as measured in accordance with EN 1426<sup>24</sup>; a branched poly(styrene-block-butadiene-block-styrene) [SBS] with 29-31 % of polystyrene content (by weight), commercially known as Kraton D1184 A; conventional lime stone filler. ATTP mineral powder was supplied by Huaian Haiyuan New Material Technology Co., Ltd. China. Melamine coated ammonium poly(phosphate) II (MAPP) was supplied by Taiyuan 2 Win Trading Co., Ltd. China.

### **Preparation of the ATTP-MAPP complex**

The surface modification (silicates to silanol) of the nano-clay mineral ATTP was achieved by treatment with 4M HCl at 80 °C under mechanical stirring for 4 hours and subsequently washing with excessive deionized water until pH neutral. To the above colloidal solution, melamine coated ammonium polyphosphate was mixed in a ratio of ATTP/MAPP (3:1) into a vessel and stirred overnight at room temperature. Next day, the mixture was filtered and dried at 110 °C for 24 hours and finally grinded in a ball-mill in order to achieve a particle size of 80-micron.

### **Introducing Bitumen**

A predetermined amount (74% by weight) of bitumen was loaded into stainless steel containers and left overnight in an oven at 110 °C. Each stainless steel container with melted bitumen was taken out of the oven and put into a container supplied with electrical heating in order to reach a temperature of approximately 200 °C. The hot bitumen was stirred with a stirring machine (Silverson L4RT) at 8000 rpm during the slow addition of SBS (8% by weight) for 10 minutes, followed by gradual addition of filler or fire retardants (18% by weight) at 1200 rpm for 15 minutes. This hot mixture was further stirred at the same speed and temperature for 30 minutes, followed by slow stirring at 100 rpm for 5 minutes in order to expel any air bubbles and to ensure homogenous dispersion of the filler or fire retardants. The hot polymer modified-bitumen with and without filler and fire retardants was casted in an iron mold of dimension approximately 250 x 100 x 2 mm (l x b x d), followed by a cooling period at room temperature. The details of the contents for the different recipes can be seen

in Table 1. We use the abbreviation B: PMB (base); C: chalk; A: ATTP; M: MAPP in the labelling of the samples.

**Table 1 Recipes for the polymer modified-bitumen with and without additives.**

<b>Recipe</b>	<b>B</b>	<b>B+C</b>	<b>B+A</b>	<b>B+M</b>	<b>B+A/M</b>
	w%	w%	w%	w%	w%
<b>Bitumen</b>	92*	74	74	74	74
<b>SBS</b>	8	8	8	8	8
<b>CaCO<sub>3</sub></b>		18			
<b>ATTP/MAPP</b>			18/0	0/18	13.5/4.5
<b>Thickness/mm</b>	2.2 ± 0.2	2.2 ± 0.15	2.3 ± 0.1	2.2 ± 0.1	2.2 ± 0.2

\*18 of the 92% represent the filler, which was bitumen in this case.

## Experimental Methods

### Rotational Viscosity

The viscosities of polymer modified-bitumen with and without additives were determined with a Brookfield viscometer (Model DV-E) according to ASTM D4402<sup>25</sup>. All the measurements were performed at 180 °C.

### Thermogravimetric analysis

The thermal stability of the polymer modified-bitumen as well as the individual ingredients was characterized using a TA instruments TGA Q500. A sample (10-20 mg) was heated at 10°C/min from room temperature to 800°C in atmospheric air while recording the mass.

### Cone Calorimetry

The tests were performed with a cone calorimeter apparatus according to the ISO-5660 standard procedures<sup>21</sup>. Polymer modified-bitumen specimens with and without additives (lime stone filler or fire retardant) of dimension 100×100×2 mm (l×b×d) were mounted on a non-combustible mineral wool base in horizontal position and covered by a stainless steel retainer frame. The sample size was 24 ± 2 g. The actual thickness was measured in several places. The data shown is representative for 2 or 3 repeated runs. The error involved in the measurements are similar to what is normally found in cone calorimetry data; that is, the errors are smaller for larger values of the parameters and an approximate 10% error is associated with the reported values<sup>26</sup>.

The specimens were subjected to an external heat flux of 15 kW/m<sup>2</sup> and a spark igniter was also introduced right above the sample surface. This relatively low external heat flux was used to allow for a better analysis and understanding of the fire retardant properties. Such a test provides a wealth of knowledge that could be used to assess a number of parameters related to the thermal response of the PMB with and without various additives. These properties include time to ignition (TTI), heat release rate per unit area (HRRPUA), peak heat release rate per unit area (pHRRPUA), time to peak heat release rate (TpHRR), total heat released (THR), total mass loss (TML) and mass loss rate (MLR).

## Scanning Electron Microscopy

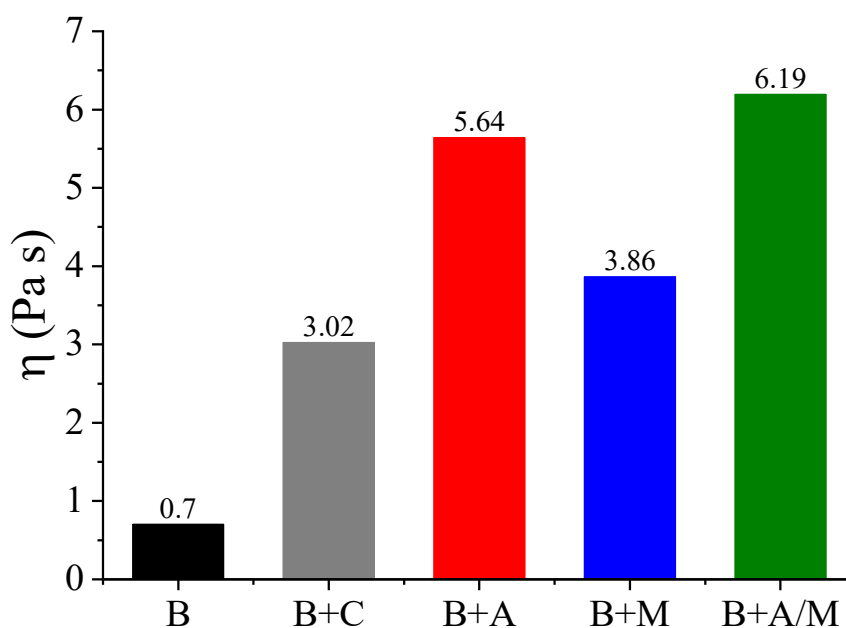
SEM images were acquired on a FEI Quanta 200 ESEM FEG (USA) under high vacuum mode ( $10^{-6}$  mbar) by using a 5 kV acquisition voltage and an Everhart-Thornley (E-T) detector was used to detect secondary electron signals. The SEM samples were produced from the exterior layer of the char residues obtained after the cone calorimetry tests. The specimens were covered with less than 10 nm conductive layer of gold prior to every measurement.

## Results and Discussion

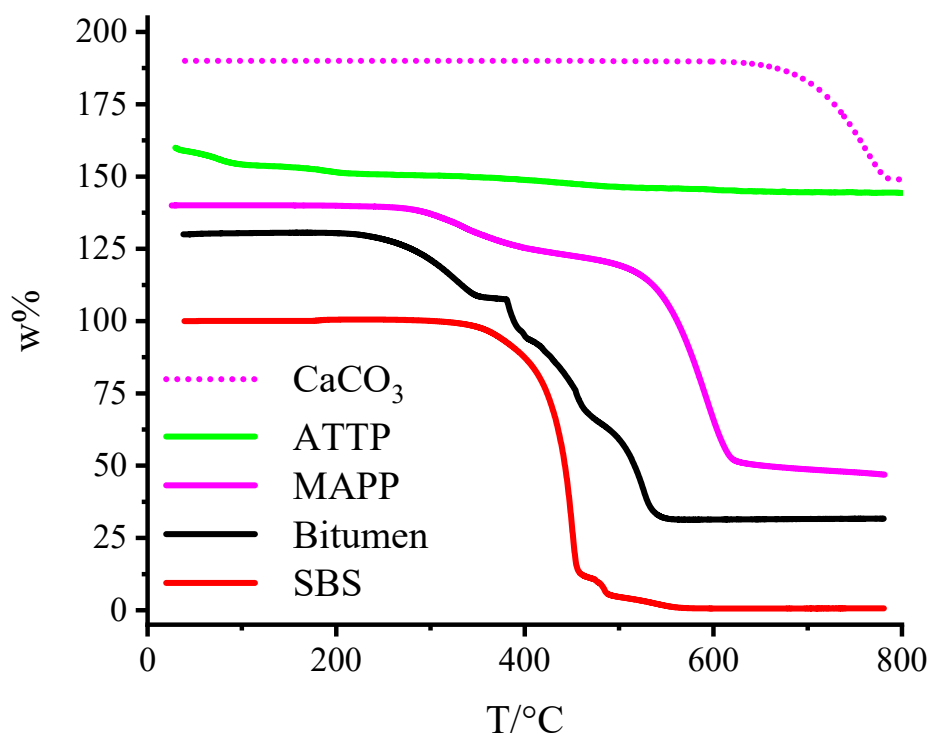
In this section, results from TGA and cone calorimeter characterization are presented and discussed. It is noted, that the present study is focussed on fire retardancy. Thus, in order to develop a roofing more issues, such as hydrolytic and UV-stability will have to be addressed.

### Rotational Viscosity

The viscosity results in Figure 1 show that bitumen containing ATTP have higher viscosity than the other additives. The viscosity of the original bitumen without any additives has the lowest value of all the samples.



**Figure 1** Viscosity at 180 °C of the different recipes used in the preparation of bitumen sheets for cone calorimetry tests.

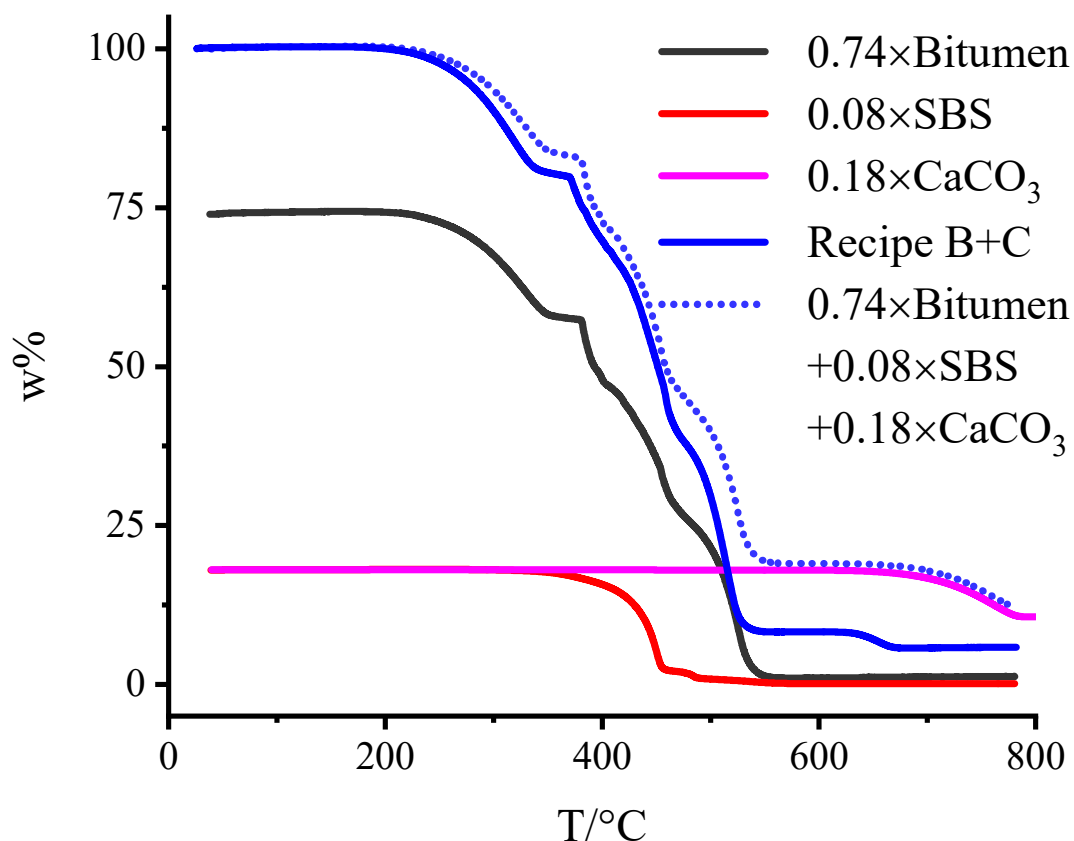


**Figure 2.** TGA of the ingredients used in the recipes. The traces have been vertically offset for clarity: SBS 0%; Bitumen 30%; MAPP 40%; ATTP 60%; CaCO<sub>3</sub> 90%. A version without offset is found in the supplementary material

## Thermogravimetric analysis

The results of the TGA are shown in Figure 2 to Figure 6. The individual ingredients behave as expected. The SBS degrades in one major process slightly above 400 °C and leave almost no residual (<1%). As mentioned in the introduction, bitumen is a complicated mixture with an equally complicated degradation pattern. It has four major degradation processes with peak mass loss rates at 330 °C, 380 °C, 450 °C, and 520 °C, presumably reflecting the four major components in the bitumen. Bitumen also leaves little residual mass (1.7% at 780 °C). The MAPP degrades in two steps at 350 °C and 600 °C, leaving only about 7% residue at 780 °C. ATTP shows a slow mass loss over the entire temperature range consistent with loss of water bound in different manners in the structure leaving a residual of approximately 84% at high temperature. Finally, CaCO<sub>3</sub> shows the expected mass loss corresponding to loss of CO<sub>2</sub> at 750 °C leaving a residual of about 60%.

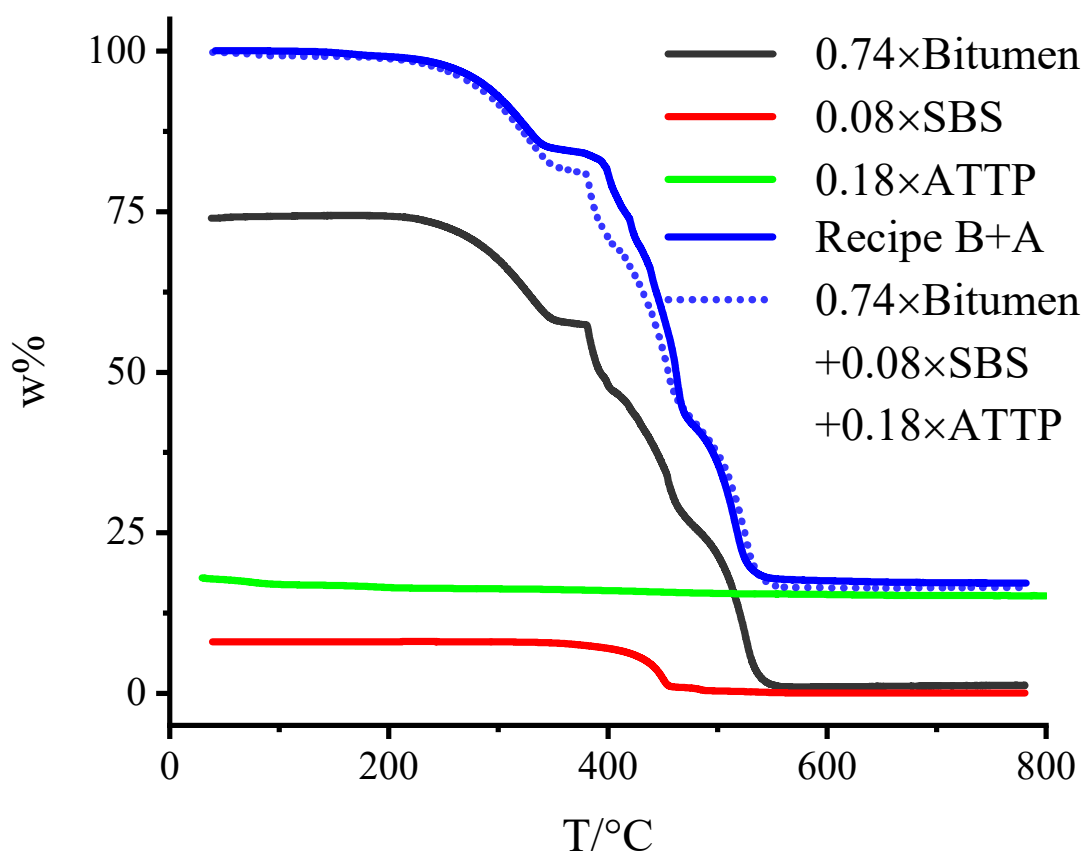
The TGA trace of Recipe B+C is almost exactly modelled by the weighted sum of the traces for bitumen and SBS (data not shown).



**Figure 3.** TGA trace of Recipe B+C (experimental: solid blue line; model: dotted blue line). The Recipe B+C model is the sum of the traces for the ingredients.

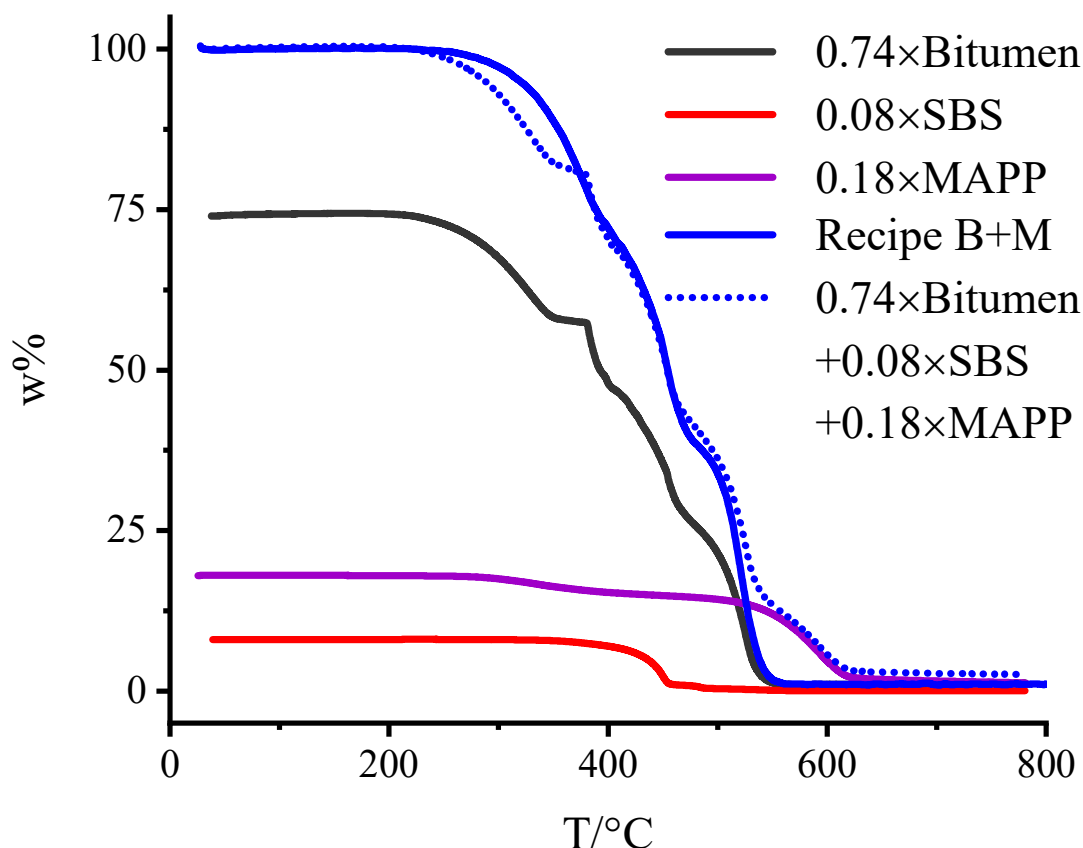
In Figure 3 the TGA traces for Recipe B+C and the components scaled to the amount found in the recipe are shown. It appears that the presence of the bitumen mixture induces the CO<sub>2</sub> loss from CaCO<sub>3</sub> to occur at a 100 °C lower temperature than in pure CaCO<sub>3</sub>. We note that the data also indicate that some of the expected residual CaO is lost. Whether this is due to a chemical process or just loss of solids from the TGA pan remains unresolved.





**Figure 4.** TGA trace of Recipe B+A (experimental: solid blue line; model: dotted blue line). The Recipe B+A model is the sum of the traces for the ingredients.

In Figure 4 the TGA traces for Recipe B+A and the components found in the recipe are shown. The trace shows a slight slowdown of the mass loss in the temperature range from 340 °C to 470 °C compared to expected contribution from the ingredients. The residual at high temperature is as expected from the contribution from the ingredients (~17%).



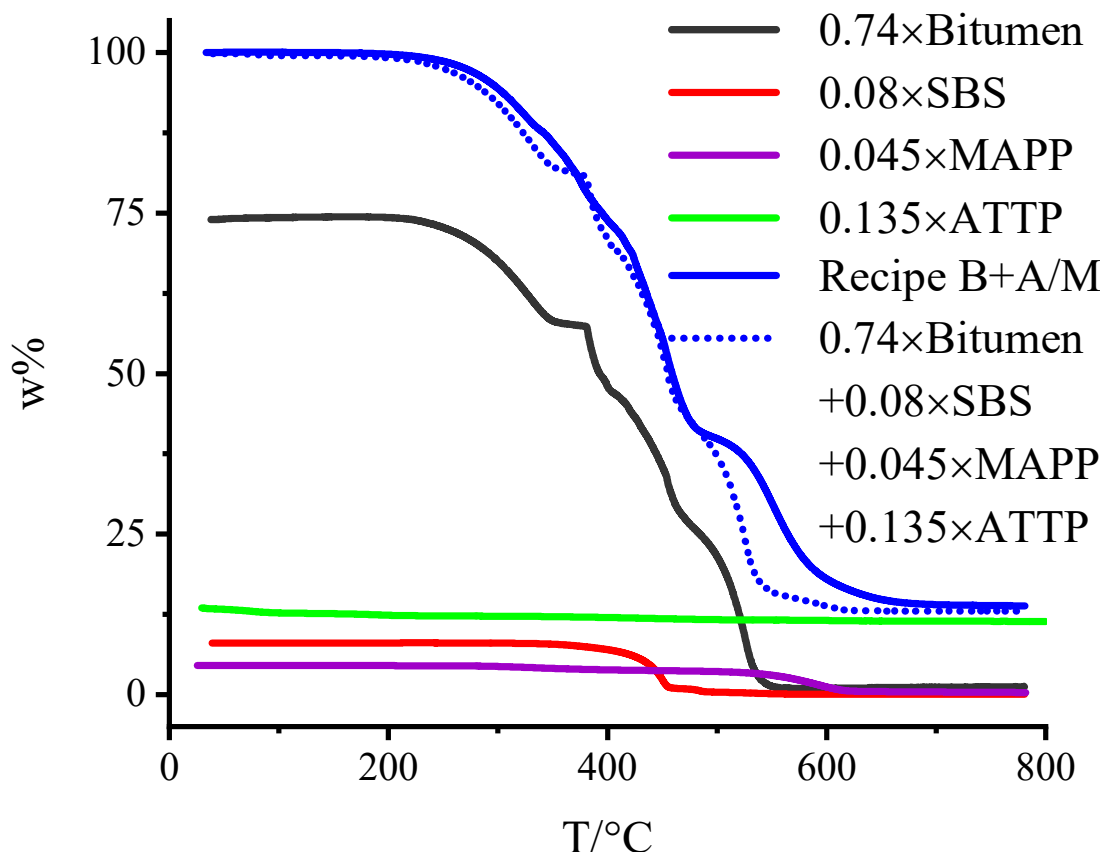
**Figure 5.** TGA trace of Recipe B+M (experimental: solid blue line; model: dotted blue line). The Recipe B+M model is the sum of the traces for the ingredients.

In Figure 5 the TGA traces for Recipe B+M and the components found in the recipe are shown. The trace shows a slight slowdown of the mass loss in the temperature range from 245 °C to 370 °C and a substantial increased mass loss from 530 °C to 620 °C compared to the sum of contributions from the ingredients. Recipe B+M leaves little residue at high temperature (~1%).

Figure 6 shows the TGA traces for Recipe B+A/M and the components found in the recipe. The trace show a slight slowdown of the mass loss in the temperature range from 245 °C to 425 °C and a substantial increase in the mass loss between 490 °C and 670 °C as compared to the sum of contributions from the ingredients. Recipe B+A/M leaves the residue at high temperature (~14%) expected from the sum of the ingredients.

Thus, the mixture of ATTP and MAPP retain the slowdowns seen for recipes 3 and 4, respectively, while suppressing the increased mass loss seen at high temperature in Recipe B+M. In conclusion, the two additives ATTP and MAPP act in synergistic manner as analyzed by TGA.

The general conclusion from the TGA data is that most of the behaviour can be understood from the properties of the individual components. However, there are a couple of exceptions. For example, the addition of  $\text{CaCO}_3$  to the B leads to two



**Figure 6.** TGA trace of Recipe B+A/M (experimental: solid blue line; model: dotted blue line). The Recipe B+A/M model is the sum of the traces for the ingredients.

processes of extra mass loss around 500°C and 650°C (Figure 3). A similar, but less prominent phenomenon, is observed for addition of MAPP where extra mass loss in recipe B+M is seen the temperature interval 530°C to 620°C (Figure 5). Finally, for addition of both ATTP and MAPP the mass loss is smaller than predicted by the model above ~480°C and most prominently in the interval 480°C to 630°C (Figure 6).

## Cone Calorimetry

The cone calorimeter results from all the experiments are shown in Table 2 and the key flammability parameters are explained in the following paragraphs. The main focus of this article is to interpret the results obtained from cone calorimetry, and therefore, the remaining part of the report is dominated by these results.

**Table 2. Summary of cone calorimeter test data for different recipes exposed to an external heat flux of 15 kW/m<sup>2</sup>.**

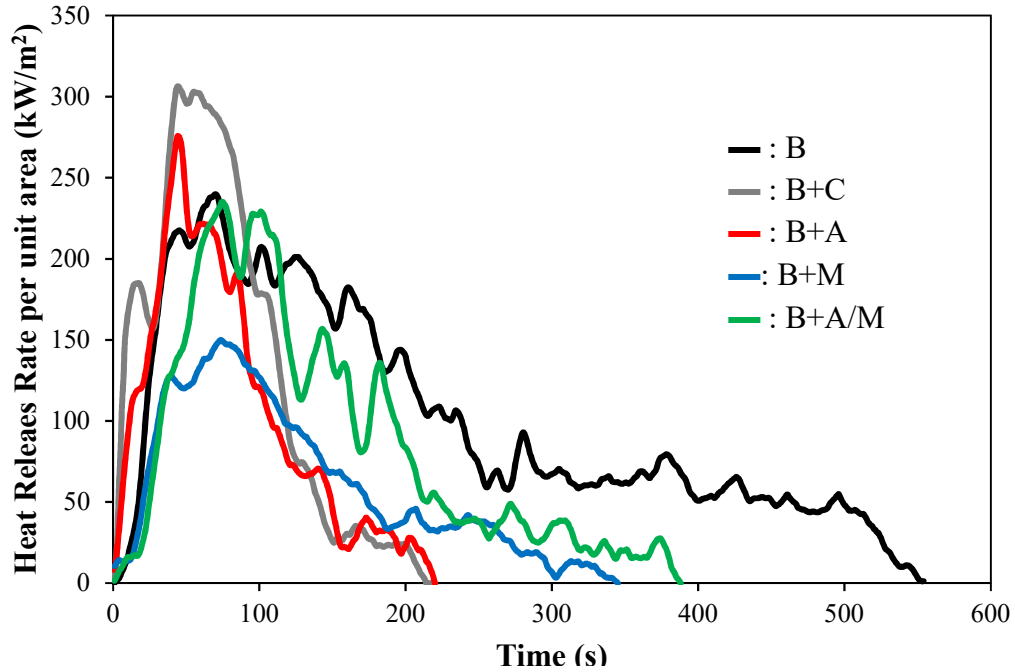
Recipe		B	B+C	B+A	B+M	B+A/M
TTI	(s)	144	142	143	121	143
pHRRPUA	(kW/m <sup>2</sup> )	246	319	290	153	242
TTpHRR	(s)	87	59	35	53	61
THR	(MJ/m <sup>2</sup> )	55.4	29.2	23.0	21.1	31.6
TML	(%)	75.7	42.9	40.2	37.4	40.0

### ***Time to ignition***

The time to ignition (TTI) is defined as the required time for a sustained flame on or above the surface of the specimen<sup>21</sup>. It was found to be in the range from 121-144 s for all the tested samples. Recipe B+M had the lowest TTI (121 seconds), while all the other recipes were in the range of 142-144 seconds, as seen in Table 2. The cluster of TTIs for recipes B, B+C, B+A, and B+A/M made it difficult to distinguish them and, therefore, it would be pointless to only use this parameter as the determining factor for the effectiveness of the fire retardants. However, a comparison of recipes B+A, B+M and B+A/M (18% ATTP, 18% MAPP, 13.5% ATTP + 4.5% MAPP, respectively) shows that the addition of pure MAPP decreases the TTI, which is a result in line with earlier observations<sup>27</sup>. As a result of replacing 3/4 of the MAPP mass (13.5% of the total mass) with ATTP, the exposure of these bitumen sheets to the external heat flux returned the TTI to the baseline for the original PMB (~144 s).

### ***Heat release rate and burning period***

The heat release rate per unit area is considered the most important parameter to study when assessing the burning behavior of a material<sup>28</sup>. The HRRPUA for the five tested recipes showed various trends that help identify the effectiveness and impact of the various fire retardants used. The heat release rate of Recipe B increased to a pHRRPUA value of 246 kW/m<sup>2</sup> followed by a long tail and, thus, a burning period greater than 9 minutes. It was visually observed that the entire surface ignited rapidly for Recipe B (Figure 7), which is in accordance with the measured steep increase in the HRRPUA curve. This is expected for a recipe without any fire retardant. This was followed by consumption of the fuel, which is illustrated by the slowly decreasing HRRPUA until the specimen self-extinguished due to fuel depletion. Among all the aforementioned recipes, with the exception of Recipe B+M, Recipe B had a lower pHRRPUA value than the literature value for experiments performed at a much higher incident heat flux (50 kW/m<sup>2</sup>)<sup>29</sup>. It was visually observed that the PMB

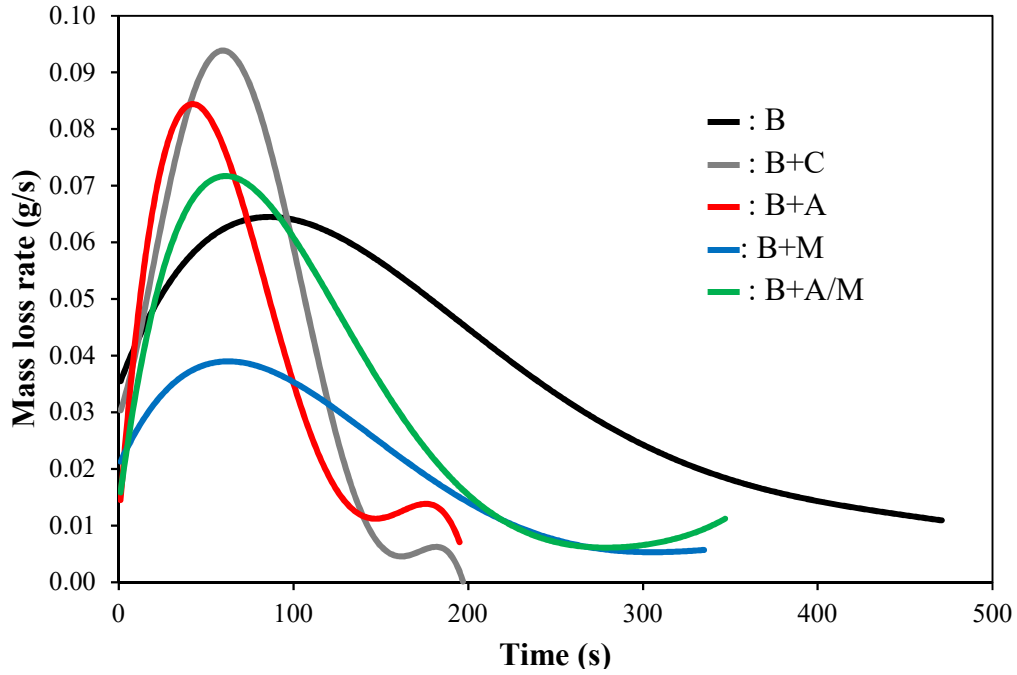


**Figure 7.** Heat release rate per unit area (HRRPUA) curves for polymer modified bitumen with and without additives exposed to a heat flux of 15 kW/m<sup>2</sup>.

transitioned to a more liquid state. As a result, a more significant fraction of energy was used for this phase transition, thus resulting in a lower pHRRPUA. This is further supported by the viscosity results shown in Figure 1, which show that Recipe B has a lower viscosity compared to all the other recipes.

The heat release rate per unit area for Recipe B+C initially grew to 181 kW/m<sup>2</sup>, followed by a slight decrease in the HRRPUA. This decrease is believed to be due to the physical presence of CaCO<sub>3</sub>. However, the value later increased to its pHRRPUA value of 304 kW/m<sup>2</sup>, indicating that this filler has either very little or no fire retardant properties (Figure 7). The HRRPUA curve for this recipe is an example of an intermediate thickness, non-charring sample with vanishing plateau<sup>28</sup> (see also Figure 11 A1), which reveals that there was very little bitumen left on the surface. It is noted that Recipe B+C has the highest pHRRPUA of all the recipes, which is somewhat surprising, and especially that it is even higher than the pHRRPUA of recipe B. While there is no obvious explanation for this phenomenon, it is in line with unexpected excess mass loss seen in the TGA trace of this recipe (Figure 3).

For Recipe B+A (addition of 18% ATTP), as seen in Figure 7, the shape of the HRRPUA curve has a steep growth until it reached its pHRRPUA value of 290 kW/m<sup>2</sup>, which is 10% lower than the reference pHRRPUA (Recipe B+C). The decreased pHRRPUA value, fast decay and extinguishment after 4 minutes was due to the presence of the ATTP that release water and formed a siliceous barrier layer on the surface that decreases the transfer of heat and thus the mass from the bitumen sheet to the flame. As the combustion proceeded, the formed protective layer



**Figure 8.** Mass loss rate (MLR) curves for polymer modified-bitumen with and without additives exposed to heat flux of 15 kW/m<sup>2</sup>.

deteriorated slowly with the release of combustible volatiles from the bitumen underneath (Figure 11 B1).

The pHRRPUA value (153 kW/m<sup>2</sup>) for Recipe B+M after the incorporation of 18% MAPP into the polymer modified-bitumen was 53% lower than that of Recipe B+C. Moreover, the shape of the HRRPUA curve shows the plateau-like behavior that is typical for char- or residue-forming materials<sup>28</sup>.

Recipe B+A/M contained 4.5% of MAPP and 13.5% of ATTP in the PMB formulation, and was prepared with the goal of getting the synergistic effect of both the additives. The main aim of this formulation was to decrease HRRPUA as compared to the original bitumen matrix as well as the CaCO<sub>3</sub> mixed bitumen. It is evident from the HRRPUA curve for Recipe B+A/M that the pHRRPUA value (242 kW/m<sup>2</sup>) was lowered when compared to both recipes B and B+C. The addition of 13.5% ATTP along with 4.5% MAPP leads to a network structure, increased the bitumen viscosity (Figure 1) and showed solid-like behavior of the bitumen matrix during the combustion. The formation of a protective barrier on the surface of the material hindered further mass loss of the fuel from the underlying layers resulting in an increase of the residual mass (Table 2). The HRRPUA curve for this recipe shows a kind of unsteady development of combustion, which was due to flashing (ignition and self-extinction) during the entire measurement period. This burning behavior indicates that there was a good synergistic effect between the rodlike mineral ATTP and the intumescent MAPP.

Recipe B+A containing 18% ATTP had a high pHRRPUA and short burning period, while Recipe B+M containing 18% MAPP had a low pHRRPUA and long burning period. Recipe B+A/M is in between Recipe B+A and Recipe B+M containing 3:1

ratio of ATTP and MAPP, such that 18% of the total mass consisted of additives in all three recipes. The 13.5 % ATTP influenced the pHRRPUA of (242 kW/m<sup>2</sup>), while the burning period was influenced by the MAPP and increased compared to Recipe B+A. It appears that a synergistic effect was present and both additives dominated a unique aspect of the whole burning process and potentially, with an optimized mixing ratio, a more beneficial synergy can be obtained and make the fire retardant even more efficient by both reducing burning period and the pHRRPUA to corresponding to recipes B+A and B+M, respectively.

The pHRRPUA and burning period results indicated that it is better to maintain 18% MAPP for the greatest effect with respect to THR and pHRRPUA while also reducing the burning period compared to the baseline recipe. However, there is room for further optimization.

### ***Total heat released and time to peak heat release rate***

As shown in Table 1, the thickness of all tested samples was 2.23±0.4 mm. As expected, there was no relationship between the thickness and the measured parameters. The flame retarding properties of the recipes is predominantly a surface phenomenon. The uniform results for different thicknesses confirm the uniformity of the distribution of the additives.

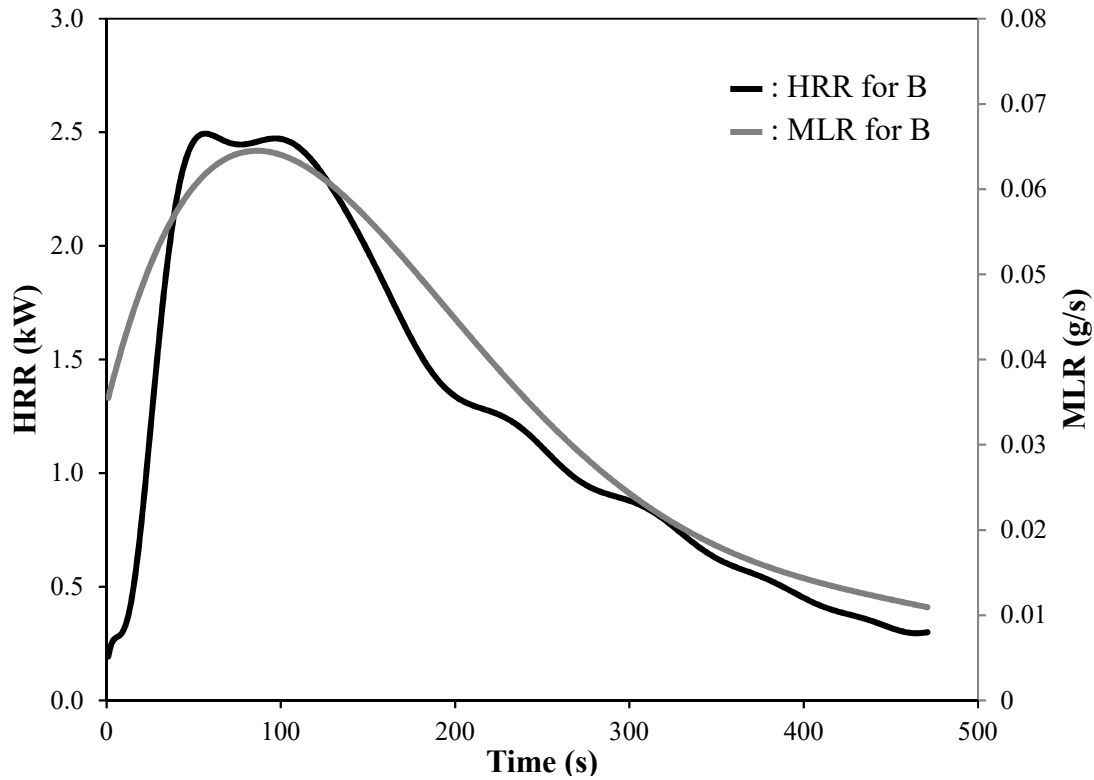
The total heat release (THR) from the different recipes was taken as the released energy from ignition until self-extinguishment. The recipes with 18% additives showed more than a 40% reduction compared to the THR of the baseline test, if the dripping or overflow behavior is neglected. The baseline released 56.4 MJ/m<sup>2</sup> and the other recipes released between 21.1 MJ/m<sup>2</sup> and 31.6 MJ/m<sup>2</sup> (recipes B+M and B+A/M, respectively). The mere replacement of fuel with an additive cannot be the sole explanation of the reduction, as the reduction was greater than 18%. As shown, the additives change the heat release (Figure 7) such that the HRRPUA decays faster after the pHRRPUA, which leads to a reduction the total burning time. All recipes containing additives show this behavior. While it was not possible to identify the dominating mechanism for this phenomenon, it is a positive effect of the replacement of bitumen with an additive. The reduced burning period can be a matter of lowering the pyrolysis to the point where sustained flaming is no longer possible. The effectiveness is different across the additives where, with CaCO<sub>3</sub> and ATTP displaying the best ability to reduce the concentration of volatiles.

### ***Mass Loss Rate, Heat Release Rate and instantaneous heat of combustion***

The MLR (Mass Loss Rate) of each specimen is shown in Figure 8. A smooth interpolation has been applied to the MLR experimental data.

As the HRRPUA is the product of the MLR and a constant (the heat of combustion), the behavior of the MLR is very similar to that of the HRRPUA, as seen in Figure 9 for Recipe B.

Another approach to evaluate the efficiency of the fire retardants is to study the instantaneous heat of combustion (Figure 10). The combustion requires energy to



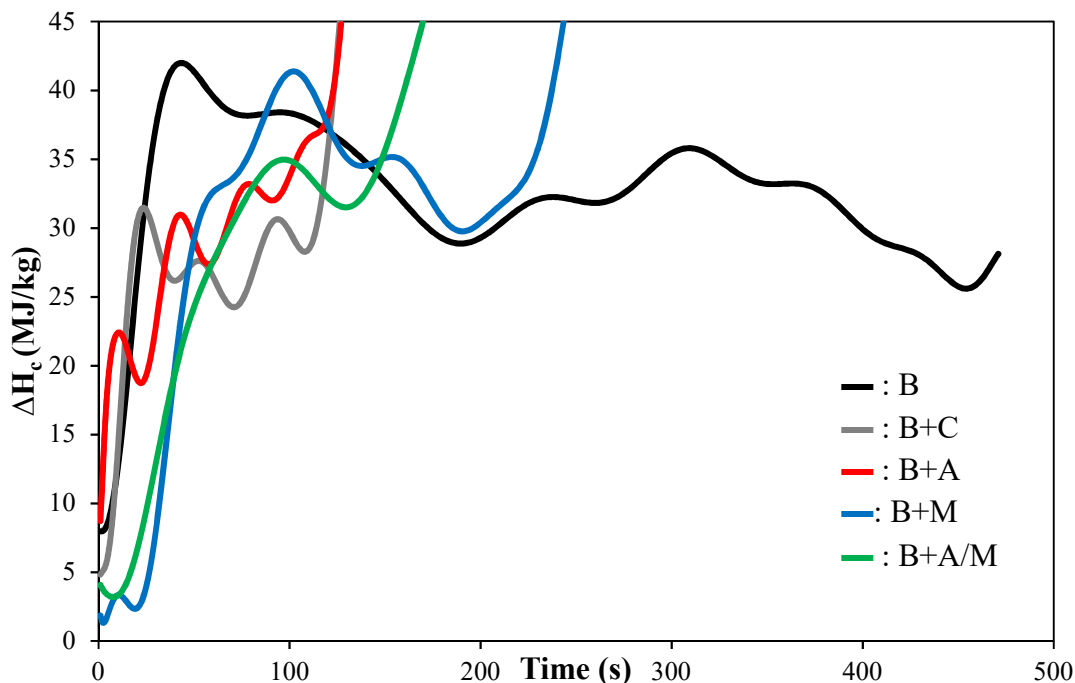
**Figure 9.** Heat release rate (HRR) and Mass Loss Rate (MLR) for Recipe B without additives exposed to heat flux of  $15 \text{ kW/m}^2$ .

transform the solid material into combustibles gases. This energy is externally provided by the radiation from the cone heater, as well as by any re-radiation from flames emerging from the specimen. The influence of the cone calorimeter source is not constant as the geometry of the flame (height, floor area) is variable. Indeed, the mean radiation extinction coefficient of a flame is strongly dependent on its geometry<sup>30,31</sup>. The ratio of the HRRPUA and MLR, i.e. the instantaneous heat of combustion<sup>30</sup>, is approximately constant for a well-established flaming combustion, which was the case in this study, according to visual observations. The observation of instantaneous heat of combustion can help identify when the sustained flaming combustion ends.

Figure 10 shows the different behavior of each recipe. Recipe B has a steady burning while the other recipes show abrupt extinctions. As such, the pure sample burns steadily, while all the other samples display that their added components lead to an earlier and more abrupt extinction. This extinction corresponds to a very high value of the heat of combustion (superior to their effective heat of combustion of  $42 \text{ MJ/kg}$ ). At the end of the combustion, a non-homogeneous burning state across the entire surface of the samples may be observed. A small residual flame translates to low mass loss rates around  $0.01 \text{ g/s}$ , which are similar to the limit of accuracy of the load cell, which causes a non-physical increase of the observed heat of combustion.

In addition, some conclusions from Figure 10 are comparable to conclusions from the HRRPUA graph (Figure 7). However, the presentation of the instantaneous heat of combustion shows also other (new or different) effects.





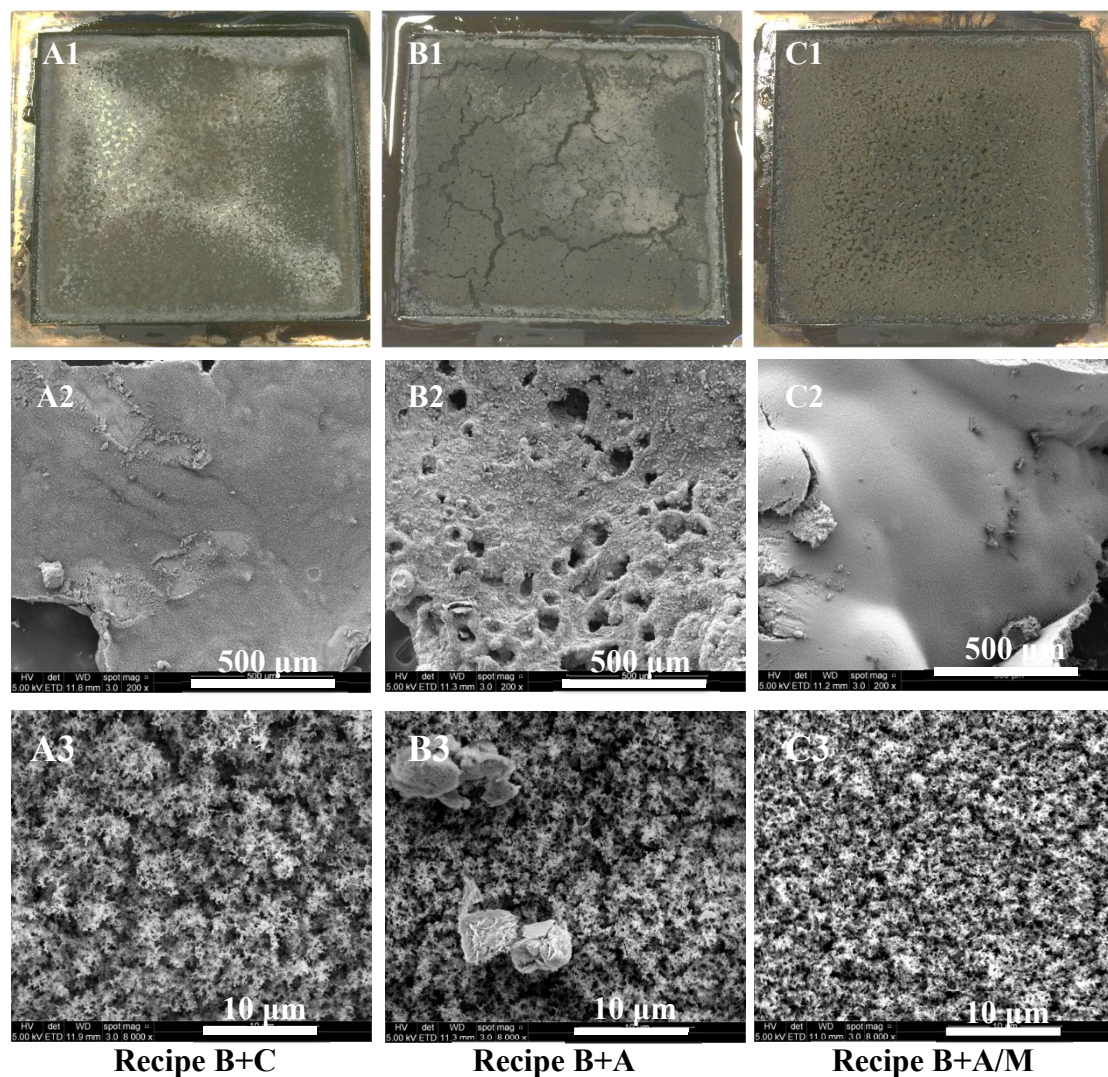
**Figure 10.** Instantaneous heat of combustion ( $\Delta H_c$ ) curves for PMB with and without additives exposed to heat flux of  $15 \text{ kW/m}^2$ .

In direct relation to the conclusions made for the HRRPUA curve, Recipe B+A has the shortest burning duration and highest heat of combustion during the first 50 seconds after ignition compared to recipes B+M and B+A/M, but does not show any distinguishable peak prior to its runaway just a continuously increasing trend.

Recipe B+A/M including both ATTP and MAPP follows the behavior of both Recipe B+A and Recipe B+M. In the initial phase, before the steady burning state, the flaming behavior is like that of Recipe B+M (corresponding to a value between 30-33 kJ/kg and showing the radical quenching property of the MAPP) but with a similar burning period of Recipe B+A.

### ***Morphological analysis of char residues***

Figure 11 shows both macroscopic (A1, B1 and C1 camera photographs) and microscopic (A2, A3, B2, B3, C2, and C3 SEM micrographs) images of char residues after the cone calorimetry tests performed on three different recipes. The images of char residues containing ATTP-MAPP (Recipe B+A/M, Figure 11C) show more compact and thick char structure compared to those containing either  $\text{CaCO}_3$  or ATTP mineral (recipes B+C and B+A, respectively). There is a general and accepted perception, based on experiments<sup>9</sup>, that heat and flammable volatiles can easily penetrate through a thin and porous char layer into the flame zone during burning, resulting in a sustainable flaming fire. On the contrary, a thick and non-porous (compact) char layer provides good barrier to both heat and flammable volatiles leading to better fire retardancy. The formation of the compact char layer for Recipe B+A/M can be ascribed to the synergistic effect between ATTP and MAPP.



**Figure 11.** Macroscopic (A1, B1 and C1) and microscopic (A2, A3, B2, B3, C2 and C3) images of char residues for three recipes after the cone calorimeter tests. A: Recipe B+C; B: Recipe B+A; C: Recipe B+A/M.

In summary for the cone calorimeter and morphological characterization all the added minerals resulted in a higher than expected decrease in the THR. The unmixed ATTP and MAPP minerals show either high pHRRPUA and early rise in the HRRPUA (ATTP) or sustained fire (MAPP). The mixed minerals ATTP/MAPP increase the TTI and especially delay the high values of the HRRPUA while good char formation is achieved and the fire is extinguished reasonably early. Thus, the positive effect of the mineral ATTP and MAPP are retained while the negative effects are suppressed.

## Conclusion

The reaction to fire of polymer modified bitumen by addition of minerals was characterized by cone calorimetry and TGA. A passive filler ( $\text{CaCO}_3$ ) and two fire retardants, ATTP and MAPP were added to the PMB at constant load in various combinations. The cone calorimeter data showed that the reaction to fire of PMB was improved with the addition of the minerals ATTP and MAPP as well as mixtures of

the two additives. Addition of all the minerals lead to substantial reduction in the total heat released. Addition of MAPP resulted in good fire retardant behavior in terms of the HRRPUA and in terms of the MLR by promoting char formation. However, there is a tendency that addition of MAPP leads to sustained burning. Addition of ATTP leads to quickly extinguished burning. However, the ATTP modification also leads to high pHRRPUA. Addition of a mixture MAPP and ATTP resulted in good synergistic effects both in terms of the HRRPUA and in terms of the MLR by promoting char formation. The synergetic action of the ATTP and MAPP minerals is supported by the TGA data that show a slow-down of the mass loss. Furthermore, the incorporation of the ATTP mineral increased the viscosity value by a factor of 6 as compared to the base bitumen, and this allows a higher temperature of application. Macroscopic and microscopic images show comparatively more retained bitumen in the recipe containing ATTP-MAPP mixture. Based on the above-mentioned results, it can be concluded that addition of ATTP in combination with MAPP has synergistic effect on the fire retardant properties of base bitumen.

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## Data

The raw data for the TGA experiments have been uploaded to zenodo.org (<https://doi.org/10.5281/zenodo.1401203>).

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